

# Infrared spectroscopy with tunable graphene plasmons: a novel route for molecular sensing

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**Abstract** Infrared spectroscopy is an important field of research as it enables sensing of molecules through the measurement of their resonances, acting as molecular fingerprints. Nanophotonics is tightly bound to this field of research as the engineering of nano-scaled plasmonic structures is crucial for enhancing the local electromagnetic field. The high local field is mainly responsible for the giant surface-induced enhancement of infrared absorption (SEIRA) and Raman scattering (SERS) by molecules in close proximity of metallic nanoparticles. These techniques have brought a number of viable, cheap and efficient commercial applications, e.g., pregnancy tests based on metal colloids [1], and promise further revolutionary applications in plasmonic sensing, although they suffer from some drawbacks. Indeed, plasmon resonances in metal-based nanoparticles are fixed by the underpinning geometric details of the plasmonic structure and lack of efficient external tunability. Besides, their spectral width can not cover the whole broad spectrum of roto-vibrational infrared transitions, and thus they enhance only few molecular resonances. Multi-frequency sensors based on subwavelength hole arrays and optical antennas have been proposed for overcoming this limitation and for achieving broadband surface-enhanced spectroscopy [2, 3]. In the last years, doped graphene has emerged as an attractive alternative to noble metals for the exploitation of surface plasmons at infrared (IR) and terahertz (THz) frequencies. Here, we develop a theoretical framework accounting for SEIRA and SERS by molecules adsorbed on graphene nano-disks. We evaluate the efficiency of these graphene-based infrared sensors finding that, thanks to the outstanding tunability of graphene through externally applied gate voltage, broadband SEIRA and SERS can be achieved. The calculated enhancement factors with respect to molecular cross-sections in the gas-phase (in the absence of graphene), are of the order of  $10^3$  for SEIRA and  $10^4$  for SERS, thus making these techniques highly appealing for sensing devices.

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[3] H. Aouani *et al.*, *ACS Nano* **7**, 669 (2013).

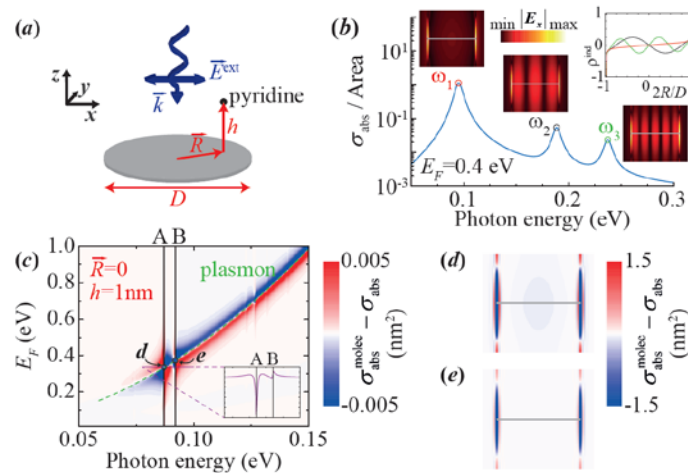


Fig. 1: (a) Sketch of the structure analyzed in this work, i.e. a graphene nano-disk of diameter  $D = 300$ nm surrounded by pyridine molecules at the coordinates  $R, h$ . (b) Absorption cross-section spectrum of the doped graphene nanodisk in the local-RPA limit with  $E_F = 0.4$ eV. Insets depict the position-dependent induced-field amplitudes and the radial profiles of the induced charge density at the three resonant photon energies  $\hbar\omega_1 = 0.10$ eV,  $\hbar\omega_2 = 0.19$ eV,  $\hbar\omega_3 = 0.22$ eV where surface plasmon modes are excited. (c) Spectral change in the extinction cross-section induced by a single pyridine molecule placed at  $R = 0$ ,  $h = 1$ nm. Labels A, B indicate the two leading absorption lines of pyridine. (d,e) Extinction cross-section map as a function of the molecule position in the  $x$ - $z$  plane for (d)  $E_F = 0.34$ eV,  $E_{phot} = 0.087$ eV, and (e)  $E_F = 0.38$ eV,  $E_{phot} = 0.092$ eV.